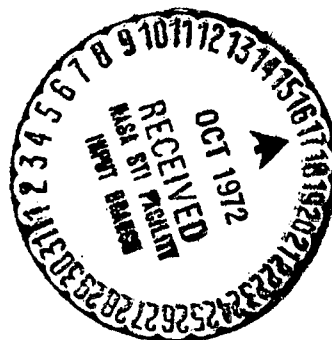


ON THE INTERPRETATION OF THE INFINITE VALUE OF THE  
DEGREE OF POLYMERIZATION ACCORDING TO CLASSICAL  
THEORY

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On the Interpretation of the Infinite Value of the Degree of Polymerization According to Classical Theory. Proposition of a New Formalism Established on Topological Grounds and for Finite Macromolecular Systems. Report<sup>(\*)</sup> by Mr. Claude M. Bruneau, presented by Mr. Georges Champetier.

The classical expressions, which in certain cases attribute an infinite value to the mean degree of polymerization by number, are shown to be advantageously replaced by a new formalism based on elementary topological considerations extracted from the theory of graphs. It leads to an axiomatic definition of the concepts of intermolecular and intramolecular bonds as well as a certain number of mean characteristic quantities, notably those measuring the importance of cyclisation.

The classical expression for the mean degree of polymerization by number of a linear macromolecular compound resulting from the chaining of bifunctional monomers is:

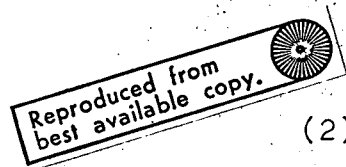
$$\overline{DP}_n = \frac{1}{1-p}, \quad (1)$$

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(\*) February 20, 1967 session.

where  $p$  is the percentage of functional groups that reacted, and is the degree of completion of the reaction. Generalized to multifunctional macromolecular systems whose monomers have a mean functionality  $f$ , it can be written as [1]:

$$\overline{DP}_n = \frac{1}{1 - p \frac{f}{2}}$$



(2)

The establishment of these formulae assumes implicitly the exclusive formation of intermolecular bonds which, on formation, ipso facto lead to a lowering of the number of molecules present by one each time. These expressions are, therefore, only valid when only intermolecular bonds form and, in this particular case, within certain limits of  $p$  corresponding to the sole formations of this type of bond. Outside these limits, the preceding relations lose all physical meaning. Thus, for values of 1 and  $2/f$ , respectively, Relations (1) and (2) take on infinite values in the mathematical sense, values that are inadmissible in the case of the finite systems usually investigated, unless one assumes that the number of molecules can be zero, which is not more admissible. Furthermore, it is observed that for values of  $p$  higher than  $2/f$  (values that may be reached physically if  $f > 2$ ) Relation (2) yields negative results.

It is possible to eliminate these anomalies if a macromolecular lattice is considered as a graph in the sense of Koenig [2], and if the elementary results of the theory of graphs are invoked.

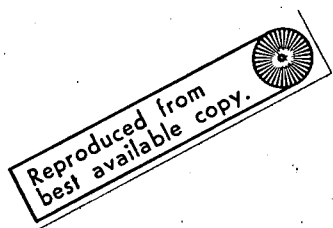
For a graph, which must not necessarily be connected, the Euler-Poincaré relation is

$$v = a - m + c$$

(3)

In this relation,  $a$  is the number of edges (chemical bonds),  $m$  the number of vertices (monomers),  $c$  the number of connected components (molecules) and  $v$  the number of linearly independent elementary cycles or cyclomatic number.

When a bond can be formed between two arbitrary functional groups (homogamic systems), calling  $m_f$  the number of f-functional monomers, Relation (3) can be written [3]:



$$v = p \frac{f}{2} \sum_f m_f - \sum_f m_f + c, \quad (4)$$

$$\frac{c}{\sum_f m_f} - \frac{c}{\sum_f m_f} = 1 - p \frac{f}{2}. \quad (5)$$

If  $v = 0$ :

$$\frac{1}{\overline{DP}} = 1 - p \frac{f}{2}, \quad (6)$$

where  $\overline{DP} = \sum_f m_f / c$  is the mean degree of polymerisation by number of a macromolecular system. One finds Relation (2) again. If  $v \neq 0$ :

$$\frac{1}{\overline{DP}} - \frac{1}{\overline{DPC}} = 1 - p \frac{f}{2}, \quad (7)$$

an expression in which  $\overline{DPC} = \sum_f m_f / v$  will be called, by analogy, the mean cyclomatic degree of polymerisation by number.

Taking into account the possible variation of  $c$  ( $\sum_f m_f$  to 1) of a ( $0$  to  $\frac{f}{2} \sum_f m_f$ ), that is of  $p$  ( $0$  to  $1$ ) and of  $v$  (whose range depends on topological constraints linked in particular to the parity of the functionality  $f$  [the parity of  $\sum_f m_f$  is assumed] and to the cyclisation of the [linear] chains exclusively made of bifunctional groups), Relation (7) is completely general within the thus allowed and delimited domain of the system structural state.

When a bond can only be formed between two types A and B of reactive sites (heterogamic systems) present in the amounts  $N_A$  and  $N_B$  of ratio  $r = N_A / N_B$ , Relation (7) remains completely valid if the further constraint

$$p = \frac{2r p_A}{r + 1} = \frac{2 p_B}{r + 1}. \quad (8)$$

is added.

For the particular value  $p = 2/f$ , the proposed Relation (7) shows that  $\overline{DP} = \overline{DPC}$ , i.e., the number of linearly independent cycles of the system, is equal to the number of molecules. If, for that value, the mean degree of polymerisation by number is not infinite but equal to the maximum allowed value ( $\sum_f m_f$  in the case of stoichiometric homogamic and heterogamic systems), the number of molecules reduces to 1 and the system displays a linearly independent cycle. The system will thus be made of only one noncyclic macromolecule (topological tree) with a mean degree of polymerisation by number

$$\overline{DP} = \sum_f m_f, \text{ if } p = \frac{2}{f} - \frac{1}{\frac{f}{2} \sum_f m_f}$$



Above that value, the degree of polymerisation cannot increase further if  $p = 2/f$  ( $p = 1$  for the so-called linear systems). The system finally composed of only one molecule will necessarily have one cycle. Later ( $f < 2$ ) as many cycles as bonds, which then must be intramolecular.

For all  $p$  values within the allowed structural state of the system, Relation (7) shows the correlation between two mean characteristic quantities. One of them  $\overline{DP}$  gives the importance of the monomer participation in molecular formation, the other,  $\overline{DPC}$ , gives the importance of the eventual participation of the monomer in cycle formation.

By suitably transforming this relation, a mean degree of cyclisation  $\overline{DC} = \nu/c$  can be defined, whose expression is

$$\overline{DC} = 1 - \overline{DP} \left( 1 - p \frac{f}{2} \right) \quad (9)$$

This relation is the formal expression of the classical method which makes it possible to show the existence of intramolecular bonds by two experimental measurements: the degree of completion of the reaction and the mean degree of polymerisation by a procedure of counting the molecules. Without a statistical study of the repartition, it does not permit us to determine the total number of

intramolecular bonds participating in a base of cycles, but only the dimensions of that base, i.e., the number  $v$  of intramolecular bonds whose suppression makes the system noncyclical — therefore, formed only of intermolecular bonds.

It seemed useful to us to propose this new formalism which, by suppressing the concept of an infinite degree of polymerisation from classical theory, which is not very suitable for finite systems, permits the concept of cyclisation to be substituted and introduced very generally on topological grounds. It leads, furthermore, to the axiomatic definition of a certain number of characteristic mean quantities, especially those measuring the amount of cyclisation, in close relation to the important concepts of intermolecular and intramolecular bonds, which have sometimes been defined and ambiguously used up to now.

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